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Controllable growth of $\text{In}(\text{OH})_3$ nanorods with rod-in-rod structure in a surfactant solution

Xian-Hua Zhang, Su-Yuan Xie^{*}, Zi-Mian Ni, Xuan Zhang, Zhi-Yuan Jiang,
Zhao-Xiong Xie, Rong-Bin Huang, Lan-Sun Zheng

Department of Chemistry, State Key Laboratory for Physical Chemistry of Solid Surfaces, Xiamen University, Xiamen 361005, China

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Abstract

The $\text{In}(\text{OH})_3$ nanorods (25–55 nm in diameter and 120–200 nm in length) bearing parallel subunit nanorods (diameters ranging from 8 to 10 nm) were synthesized by controlling hydrolysis of indium nitrate in the presence of hexamethylene tetraamine and cetyltrimethylammonium bromide.

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Keywords: Nanorods; Indium hydroxide; Surfactant; Template

Nanosize indium hydroxide is a kind of interesting material due to its special semiconducting and optical properties. Ishida and Kuwabara [1] reported that conductivity of $\text{In}(\text{OH})_3$ thin films varied with the experimental conditions in the range of 10^{-7} – 10^{-3} S/cm², which is typical for wide band gap semiconductor. Gedanken and co-workers [2] estimated the optical band gap, E_g , was 5.15 eV from the diffused reflectance spectroscopy (DRS) spectra and the Kubelka–Munk (K–M) spectra of some needle-like nanoparticles of indium hydroxide. Several synthesis methods, such as sonohydrolysis [2], peptization of colloidal precipitates [3], and double-jet precipitation [4], have been developed for the preparation of nanosize indium hydroxide with different morphologies. Although template-directed methods, including assemblies of surfactants (soft-template) [5–8], and channels in porous materials (hard-template) [9,10], have represented a straightforward approach toward a variety of nanostructures, this template process has scarcely been applied to preparation of $\text{In}(\text{OH})_3$. Here, we reported an effort to employ the

surfactant template for controllable synthesis of $\text{In}(\text{OH})_3$ nanostructures, in which indium nitrate was hydrolyzed in the presence of hexamethylene tetraamine (HMT) and cetyltrimethylammonium bromide (CTAB).

20 ml of 0.02 dm^{-3} $\text{In}(\text{NO}_3)_3$ and 20 ml of 0.02 mol dm^{-3} HMT solutions were mixed in a flask with appropriate quantity (e.g., 1.46 g) of CTAB. Heated to about 80 °C and stirred slowly for 3 h, the mixture solutions would undergo hydrolysis reaction to produce white precipitations of $\text{In}(\text{OH})_3$, which were repeatedly centrifugated and washed for five times to remove the remained surfactant (CTAB) for further characterizations.

Transmission electron microscopy (TEM) micrographs were taken using a JEM-100CXII Transmission Electron Microscope, field-emission scanning electron microscopy (SEM) images were taken using a LEO1530 SEM system, and high-resolution TEM (HRTEM) images were obtained on a TECNAI F-30 FEG TEM. X-ray powder diffraction (XRD) was carried out on a Rigaku DMAX/RC X-ray Diffractometer using Cu K α radiation ($\lambda = 0.154178 \text{ nm}$).

The experimental results revealed that controllable growth of $\text{In}(\text{OH})_3$ nanorods were difficult to be realized under relatively high temperature (100–140 °C) and high

^{*} Corresponding author. Tel.: +865922185191; fax: +865922183047.
E-mail address: syxie@jingxian.xmu.edu.cn (S.-Y. Xie).

reactants concentrations ($>0.05 \text{ mol dm}^{-3}$). Therefore, the hydrolysis reaction was carried out at relatively gentle reaction conditions, i.e., moderate temperature (80°C) and proper reactants concentrations (0.01 mol dm^{-3} indium nitrate and 0.01 mol dm^{-3} HMT), for evaluating the growth of the $\text{In}(\text{OH})_3$ products under varying quantity of the surfactant CTAB.

Fig. 1 shows the TEM images of the products synthesized under different quantities of CTAB as well as optimal temperature and reactant concentrations conditions. Elliptical particles of $\text{In}(\text{OH})_3$ with minor axis of about 180 nm and long axis of about 400 nm dominated over the products on absence of the surfactant (see Fig. 1(a)). When 0.49 g CTAB was added, elliptical $\text{In}(\text{NO}_3)_3$ nanoparticles with minor axis of about 90 nm and long axis of about 150 nm were obtained, accompanying with a few of needle-like $\text{In}(\text{OH})_3$ nanocrystals (see Fig. 1(b)). Increasing the CTAB amount to 1.17 g, the elliptical $\text{In}(\text{NO}_3)_3$ nanoparticles were altered to cubic nanoparticles (see Fig. 1(c)). Going on to increase the CTAB up to 1.46 g, the ratio aspect of the cubic products increased dramatically to form $\text{In}(\text{OH})_3$ nanorods with diameters ranging from 25 to 55 nm (mean 40 nm) and length up to 200 nm (see Fig. 1(d)). These results indicated that the surfactant template played a key role on alteration of shape and size of the $\text{In}(\text{OH})_3$ product in the hydrolysis reaction. As the concentration of the surfactant increases, it seems that the shape of the micelle in solution tends to alter from sphere to rod, resulting

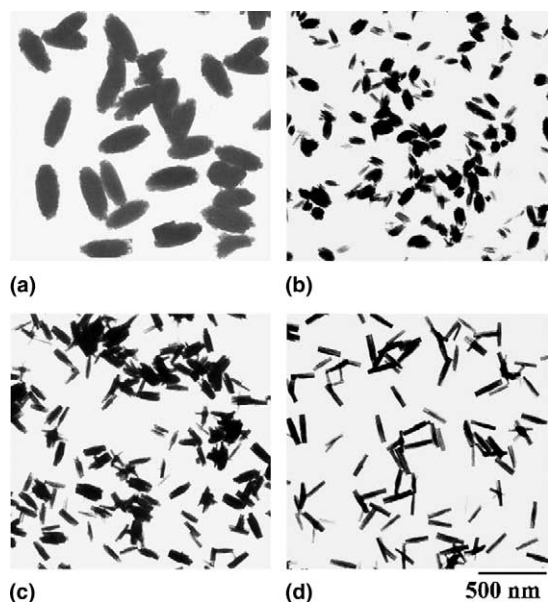


Fig. 1. TEM images of the $\text{In}(\text{OH})_3$ nanostructures produced in the presence of CTAB with different quantity: (a) 0 g; (b) 0.49 g; (c) 1.17 g and (d) 1.46 g.

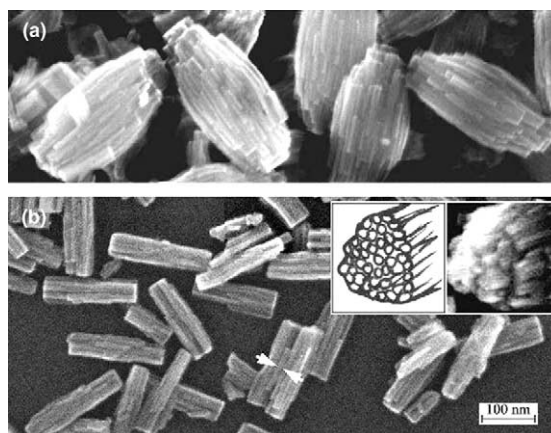


Fig. 2. (a) SEM image of $\text{In}(\text{OH})_3$ elliptical particles; (b) SEM image of the $\text{In}(\text{OH})_3$ nanorods, the inset is a magnified ($4\times$) image of a cross-sectional end and its model.

in the different shapes of $\text{In}(\text{OH})_3$ products as shown in Fig. 1.

SEM images showed that the $\text{In}(\text{OH})_3$ particles and nanorods grown under different conditions were assembled by rod-like subunits (see Fig. 2), and the lateral dimension of subunits is about 8–10 nm (arrow marked in Fig. 2(b)). While the elliptical particles bear a number of nanorods with different length (see Fig. 2(a)), the nanorods are the aggregation of subunits with almost equal length. The inset in Fig. 2(b) shows an end belonging to one of the $\text{In}(\text{OH})_3$ nanorods. Considering the lateral diameters of this nanorod (about 52 nm) and its subunits (8–10 nm), it was mathematically evaluated that the rod-in-rod nanostructure was organized from about 26–40 nanorods. Unfortunately, the present experiments are not enough to testify the relationship between surfactant and bundle structure.

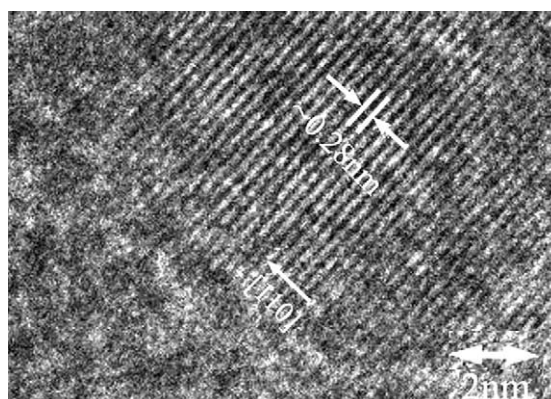


Fig. 3. HRTEM image of a $\text{In}(\text{OH})_3$ nanorod subunit.

Further insight into the $\text{In}(\text{OH})_3$ nanostructures could be revealed by HRTEM image of the rod-like $\text{In}(\text{OH})_3$ subunit. As shown in Fig. 3, the fringe spacing (~ 0.28 nm) matches well with the separation between (220) lattice planes, implying growth of the subunit is along the [110] direction. XRD pattern of the as-prepared $\text{In}(\text{OH})_3$ nanorods is assigned to the cubic $\text{In}(\text{OH})_3$ (JCPDS card No. 16-0161).

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